The most noticeable feature in Fig. 2 is the systematic error present in the linear analysis (eq. [4]). Only for pure water does the linear relationship appear to give a random error. The fact that systematic errors appear in this function suggests that it is not a reliable representative function of the present data. The second order polynomial. the Benson–Berson equation, and the incremental slope analysis (eqs. [6], [8], and [9]) all appear to give random scatter about zero. The only exception is in the Benson–Berson equation for 0.4 mole fraction ethanol. A further comparison of the four functions is shown in Table IV where the standard deviations are reported.

In accord with the above suggestion, function [4] gives a relatively large standard deviation, whereas eqs. [8] and [9] have values about twice that of eq. [6]. From the data presented in Fig. 2 and Table IV, it is evident that the quadratic function (eq. [6]) best represents our data. It must be emphasized that although we conclude the most reliable function for our data to be a second order polynomial, it need not be generally applicable to all reactions. However, by analogy, we would consider it to be generally applicable to ionic unimolecular decompositions.

TABLE IV

Standard deviation of each function

Function	Number of points	Standard deviation	Relative values
[4]	24	0.0814	4.24
[6]	24	0.0192	1.00
[8]	19	0.0374	1.94
[9]	19	0.0420	2.19

Physical Significance

We have, so far, indicated the empirical merits of various methods of handling kinetic pressure data. An analysis of the physical significance of each would be useful.

The first order polynomial (eq. [4]) ignores the fact that the transition state and substrate may have different isothermal compressibilities. Consequently, the inadequacy of this function in giving a good fit for our data is not unexpected (although Burris and Laidler (8) have found that a linear plot is satisfactory for some S_N2 reactions of ionic species). The use of a second order polynomial recognizes that $(\partial \Delta V^*/\partial p)_T \neq 0$, but requires that $(\partial^2 \Delta V^*/\partial p^2)_T = 0$.[3]

The question arises as to whether our data are precise enough to allow a meaningful calculation of $(\partial \Delta V^*/\partial p)_T$. It is readily seen that (see eqs. [6] and [1])

[12] $$(\partial \Delta V^*/\partial p)_T = -2RTC.$$

For the systems considered in this paper the percent deviation of this derivative (see *Precision Analysis*) lies between 2 and 41%. The actual values of the derivatives and their deviations are presented in Table I.

A good fit of the Benson–Berson equation (eq. [8]) is perhaps not to be expected. Benson and Berson point out that the exact pressure dependence of the rate constant reflects the change in activity coefficient as well as the change in volume during the

[3]It is true, of course, that $(\partial^2 \Delta V^*/\partial p^2)_T$ is not generally zero. The compressibility of a real substance is known to be pressure dependent (13) so that $(\partial^2 V/\partial p^2)_T \neq 0$. It would be fortuitous indeed if two states had the same value for this derivative, especially when the polarities of the two differed markedly. Since the polarity of the initial state in the present reaction is practically negligible when compared with that of the transition state, it is not to be expected that the two states have the same value for $(\partial^2 V/\partial p^2)_T$. Hence the difference in the values of this derivative cannot be zero, i.e. $(\partial^2 \Delta V^*/\partial p^2)_T \neq 0$.

activation process (4). For ionic reactions in water the authors demonstrated that the term due to the activity coefficients is negligibly small, but may become important in solvents of lower dielectric constant. For nonionic reactions, for which this term is zero, these authors used the Tait equation (10) to represent the compressibilities of both the initial and transition states of the reaction (4). This led to the development of eq. [8]. Since this function was developed for nonionic reactions, it appears fortuitous that it gives reasonable results when applied to the analysis of our data for an ionogenic reaction. However, the activity coefficient contribution to $(\partial \ln k/\partial p)_T$ can be shown to be negligible for the systems considered here.

The incremental slope analysis (eq. [9]) was seen to give ΔV_0^* values which coincide with the second order polynomial (Fig. 1). As stated previously, this is because they both allow for the same pressure dependence of ΔV^*. That this is true can be shown by taking the limit of infinitesimal increments and integrating eq. [9] at constant temperature. Thus there is no "a priori" advantage to using one of these methods over the other. However, eq. [6] reproduces the experimental data better than eq. [9] within a factor of two (Table IV). It may be noted that eq. [6] is a strictly analytical function, whereas eq. [9] becomes an analytical function only when the increments become infinitesimal. Therefore, it is not surprising that the two functions do not give identical results. It should also be noted that the incremental slope analysis may suffer from excessive amplification of the effect of the experimental uncertainties in the rate determinations when rate and pressure intervals used become small. Each k and p in the $\ln (k_{n+1}/k_n)$ and $(p_{n+1} - p_n)$ terms has an experimental error associated with it which is independent of the value of the difference between the logarithmic rates and pressures used in each term. Accordingly, as the rate and pressure intervals used become smaller the value of the experimental uncertainties in k and p approach the value of the differences, and increasing scatter of points in the plot of $\ln (k_{n+1}/k_n)/(p_{n+1} - p_n)$ versus $(p_{n+1} + p_n)/2$ is to be expected. This situation is analogous to that which results if one attempts to evaluate enthalpies of activation from two rate determinations at temperatures that are relatively close together. A similar argument was used by Benson and Berson (4) when they neglected the low pressure rates in their study of Walling and Peisach's data for isoprene dimerization (3) because of large scatter. For these reasons, and because eq. [6] is more convenient in that it lends itself to a precision analysis of the type described below, we prefer the quadratic function to the incremental slope analysis.

Precision Analysis

The functional dependence of the rate of benzyl chloride solvolysis on pressure having been established, the next step is to establish the precision of the derivatives. Since we have shown that eq. [6] is the desirable function it is necessary to determine the maximum deviations of the constants. It is convenient to determine these deviations by differentiation (14). By use of the least square functional forms of A, B, and C (eq. [6]), the deviations are given by [13] where f, g, and h are the least square functions for A, B, and C respectively.

$$dA = \sum_i \left(\frac{\partial f}{\partial k_i}\right)_{p_j} dk_i + \sum_j \left(\frac{\partial f}{\partial p_j}\right)_{k_i} dp_j$$

[13]
$$dB = \sum_i \left(\frac{\partial g}{\partial k_i}\right)_{p_j} dk_i + \sum_j \left(\frac{\partial g}{\partial p_j}\right)_{k_i} dp_j$$

$$dC = \sum_i \left(\frac{\partial h}{\partial k_i}\right)_{p_j} dk_i + \sum_j \left(\frac{\partial h}{\partial p_j}\right)_{k_i} dp_j$$